Magnetron sputtering and laser patterning of high transition temperature Cu oxide films

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High T_c Y-Ba-Cu-O films have been prepared by dc magnetron sputtering of metal alloy targets. To circumvent the negative ion effect, two alloy targets, YCu and BaCu, are sputtered in an argon atmosphere with an oxygen spray near the substrate. Films deposited on sapphire with onsets at 92 K and a 6° transition width (10–90%) have been achieved using this technique. These films have been successfully patterned with the technique of laser ablation.

Several techniques of depositing thin films of the YBaCuO superconductor have been described recently including electron beam,[1–3] laser deposition,[4] and sputtering.[5] One common technique is to sputter from a single target of $YBa_2Cu_3O_7$. However, the negative ion effect due to the high concentration of oxygen causes significant resputtering from the substrate and hence a low deposition rate.[6] The negative ion effect on sputtering perovskite oxides is well documented in the literature.[7,8] Another approach is to sputter from metal targets; however, barium metal targets are extremely difficult to work with because of its rapid reaction with oxygen and water vapor when exposed to air. We decided to use two binary alloy targets made of Ba(0.5)Cu(0.5) and Y(0.5)Cu(0.5) because BaCu and YCu are stable compounds.[9] In addition, varying the relative sputtering rates of the two targets will yield $Y_xBa_{1-x}Cu$ where x is determined by the ratio of the rates. For example, sputtering BaCu at twice the rate of the YCu will yield the 1-2-3 ratio of Y-Ba-Cu. Although the BaCu alloy is stable in the atmosphere, a thin oxide does grow on the target. This oxide can be removed with a quick presputtering. Oxygen is incorporated into the film by spraying it onto the film at a rate low enough so that the system is not flooded and the negative ion effect is avoided.

A schematic of the sputtering system is shown in Fig. 1. Two 5.0 cm targets are placed 12 cm from a rotating substrate holder. A shutter is placed between the target and the substrate holder and an oxygen spray is placed 2 cm in front of the substrate holder. The oxygen spray is a copper tube with small holes for spraying oxygen directly onto the substrates. Films are deposited on sapphire substrates at room temperature. Best results were obtained with a partial pressure of 0.2 μm of oxygen and 10 μm of argon and with a combined deposition rate of approximately 4 Å/s. The oxygen partial pressure was measured before sputtering because it dropped to an immeasurably small value during deposition due to the strong gettering effect of these materials. Sputtering from the BaCu target at twice the rate from the YCu gives films close to the Y(1)Ba(2)Cu(3) stoichiometric composition. To obtain good uniformity across the 12 cm substrate holder it was rotated at 1 cps during deposition. The uniformity as measured by resistivity is better than 70%. For the films deposited at room temperature it is necessary to perform a post-sputter anneal at 400 °C *in situ* in oxygen to passivate the film against reaction with water vapor before exposure to the atmosphere. After removal from the chamber a second higher temperature (900 °C) anneal is required to form the high T_c phase. This annealing procedure is similar to the process described by Laibowitz *et al.*[1]

An example of resistance versus temperature for a film prepared using the technique described above is shown in Fig. 2. This film is 1.6 μm thick, has an onset at 92 K and a 10–90% transition width of 6 K. The resistive transition, room-temperature resistance, and morphology of the film depend strongly on the annealing conditions and initial oxygen content of the films. The best films have a preanneal sheet-rho resistance of 2–5 MΩ/□ and a post-anneal sheet resistance less than 10 Ω/□. The composition of the films as determined by inductively coupled plasma atomic emission spectrometry[10] can be reproducibly deposited within 5% of the Y(1)Ba(2)Cu(3) composition. For some annealed films substantially off the 1-2-3 stoichiometry, the chemical analysis indicates a segregation of material during the film growth. There are usually two components, the first, Y(1)Ba(2)Cu(3) dissolves quickly in 25% HCl while the second component identified as primarily copper oxide dissolves much slower. These results have been corroborated by x-ray diffraction analysis which identified the orthorhombic perovskite phase with a certain amount of copper oxide present. Even for our best film a very small amount of copper oxide is present presumably due to the fact that our sputtering method tends to produce slightly copper-rich films.

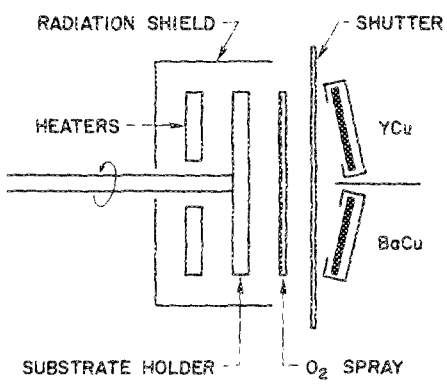

FIG. 1. Schematic showing the sputtering system.

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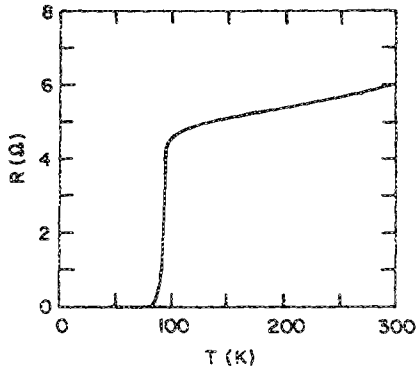
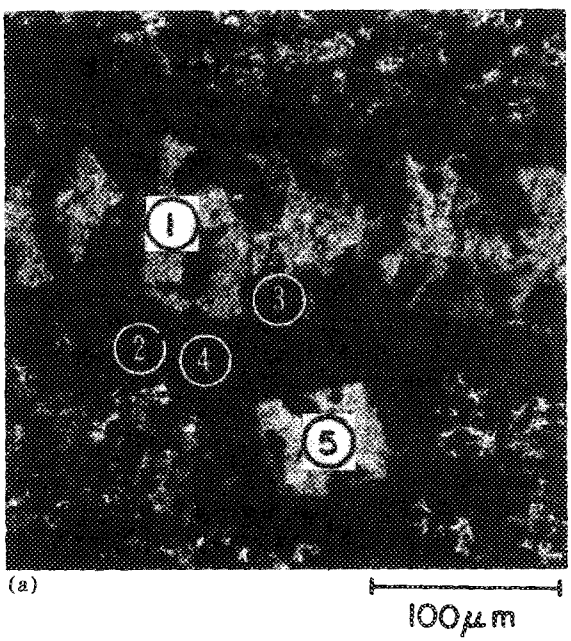
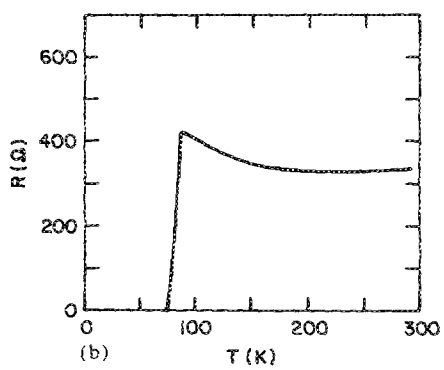


FIG. 2. Resistance vs temperature. The film is 1.6 μm thick deposited on sapphire.

It is well known that control of the composition is important to achieve sharp superconducting transitions. Some of the early samples were not stoichiometric, hence the film did not show a sharp transition. However, on one particular sample a linear chain of the Y(1)Ba(2)Cu(3) was formed accidentally. This sample allowed us to identify the morphology of the high T_c phase. The composition of the chain and several sites near the chain were analyzed with electron beam x-ray microanalysis. Figure 3(a) shows a portion of the linear formation and the analyzed regions. The linear chain, region 1, is the Y(1)Ba(2)Cu(3) compound. The resistive transition of the chain [Fig. 3(b)] was sharp with an onset at 90 K. The region around the chain was insulating at room temperature. Although the morphology of the films varies significantly with annealing conditions, the best films show structure similar to what was observed for this linear chain.



(a)



(b)

FIG. 3. (a) Linear chain of high T_c material is the light region which stretches across the micrograph. The width of the chain is approximately 100 μm. Microprobe x-ray analysis of the relative metal composition of the labeled sites is as follows. Site 1 located on the linear chain has a ratio of Y-Ba-Cu of 1-2-3. Sites 2, 3, and 4 are nearly identical with an average ratio of 1-1-4. Site 5 with a ratio 1-1-10 is most likely a crystal of CuO. (b) Resistance vs temperature of the linear chain in (a).

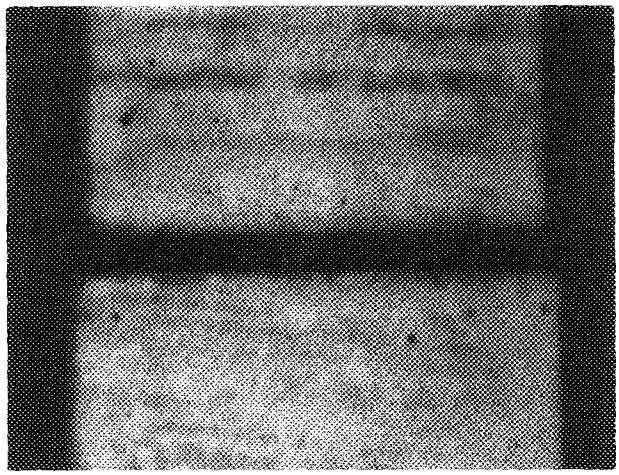


FIG. 4. 80-μm-wide film patterned using laser ablation.

For potential applications in electronic devices and for many electrical measurements it is important to pattern the films. We have shown that this can be done by laser ablation[11] with little or no degradation of the film properties. Figure 4 shows an 80 μm line formed by laser ablation. The film was 1.6 μm thick on sapphire. An excimer laser at 248 nm and a fluence of 0.86 J/cm^2 was used to ablate the film. Contact masks were used to define the pattern. Lines as narrow as 30 μm can be easily formed using a contact mask. The resistance as a function of temperature for the film before patterning and for the line after patterning is shown in Figs. 2 and 5. Small differences between the two curves may be attributed to either nonuniformities in the film or the ablation process. The critical current density of this line was

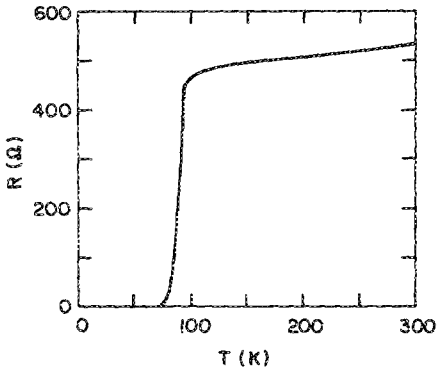


FIG. 5. Resistance vs temperature of line after laser patterning. The film is 1.6 μm thick on sapphire. The line is 80 μm with a critical current density of 500 A/cm^2 at 4.2 K. The resistance vs temperature of film before laser patterning is shown in Fig. 2.

measured to be 500 A/cm^2 at 4.2 K. This low value is presumably due to the grain boundaries of the film.

The major advantages of laser ablation technique are twofold. First, the process is very quick, taking less than a minute to ablate 1.6-μm-thick film. Second, laser ablation requires none of the wet processing associated with conventional lithography. Thus the possibility of film degradation due to chemical reaction is minimized. Ablation has been successfully tried at wavelengths 0.308, 0.248, and 0.193 μm for patterning this material. The practical linewidth obtainable with this technique has yet to be explored but may be limited by the amount of melting which occurred at the edge of the ablated region. No attempt has been made to optimize the ablation conditions in this work. Smaller and more complicated structures can be patterned using projection techniques for pattern definition.

In conclusion, it has been demonstrated that high quality YBaCuO films can be sputtered from metal alloy targets. The negative ion effect is minimized. High sputter rates and good global homogeneity over a large area have been achieved. Laser ablation has been demonstrated to be a useful technique for patterning oxide films with no serious adverse effects.

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